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(54) HYDROGEN STORAGE MATERIALS

WASSERSTOFFSPEICHERMATERIALIEN

MATIERES PERMETTANT L'ACCUMULATION D'HYDROGENE

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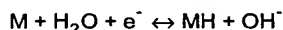
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Description

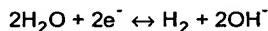
[0001] The present invention relates to a novel hydrogen storage material; a process for preparing the same; and its use in improving hydrogen transfer during charge and discharge conditions such as those required for battery electrode application.

[0002] Rechargeable batteries or secondary cells have been available for many years and include lead-acid accumulators, car batteries and, more recently, Ni-Cd cells. Efforts to improve the performance of lead-acid batteries have been effective in many respects, but the basic cell still uses lead with its environmental penalty and high density. Similarly, although Ni-Cd cells have a long lifetime, they use cadmium, which is potentially toxic and therefore also raises many environmental concerns. The demand for rechargeable batteries is ever increasing with the proliferation of portable electrical equipment such as mobile telephones, laptop computers, video cameras, power tools, garden equipment etc, also aircraft batteries, and with the prospective development of electric road vehicles.

[0003] There are many potential cell systems which have been evaluated for use in rechargeable batteries and one of the more popular ones uses hydrogen storage materials as an electrode. These are based on the ability of some metals or metal alloys to store hydrogen (in molecular, atomic or ionic form) within the metal lattice. The most commonly-used hydrogen storage material is a metal hydride. Typically, the metal hydride hydrogen storage electrode is the negative electrode in such a system, wherein the metal (M) is charged by the electrochemical absorption of hydrogen and the electrochemical evolution of a hydroxide ion:



Metal hydride batteries depend on a reversible reaction as follows:



[0004] Since the hydrogen storage material functions both as an electrode and as a store, it must be capable of efficiently carrying out several different functions: *ie* reversibly storing large quantities of hydrogen; rapidly transferring hydrogen across the surface interface during both charge and discharge conditions; and maintaining the rate of hydrogen pick-up and supply to maintain the voltage, this being dependent upon the diffusion of hydrogen through the hydrogen storage material and the rate of surface transfer. It must also be capable of charge transfer rates to match current voltage requirements of the battery; being rechargeable over many cycles without loss of performance, which requires chemical stability, even in overcharge conditions; being physically durable; being cost-effective and being non-toxic.

[0005] Amongst the main factors affecting the life and performance of a hydrogen storage material electrode, degradation of the hydrogen storage material leading to loss of its ability either to transport hydrogen and/or charge is important. This loss of ability has been linked to chemical instability where the metallic material becomes contaminated or oxidised. Oxidation can occur by the action of OH⁻ groups, or by the generation of O₂ during charging or overcharging. The oxide formed on the surface of the hydrogen storage material offers a barrier to both hydrogen and charge transfer, thus degrading performance.

[0006] Considerable research has been carried out to attempt to overcome the problems of degradation of these hydrogen storage materials. At present there appear to be two approaches: the first involves mixing the hydrogen storage material, *eg* a powdered alloy of nickel with another metal such as copper, nickel, cobalt, gold or carbon powder plated with platinum (Züttel *et al*, Journal of Alloys and Compounds, 206 (1994) 31-38), and compressing the powders to form a pellet. The second approach involves coating the hydrogen storage material particles with one or more complete coatings of metal. For example, Chen *et al* (J. Mater. Res., 9 (7) (1994) 1802-1804) describe coating fine powders of LaNi_{3.8}Co_{0.5}Mn_{0.4}Al_{0.3} with nickel, which led to improved performance of the alloy electrode. Geng (Journal of Alloys and Compounds, 215 (1994) 151-153) describes continuous-coating an alloy powder with Pd and Ni-Pd. It was demonstrated that Pd and Ni-Pd completely covering the alloy powder surface were effective in improving the discharge capacity and cycle lifetime. However, when the Pd-coated alloy powder was also plated with Ni, the Ni densely covered the alloy powder surface, which made the activation of the alloy electrode difficult. Yunshin *et al* (Journal of Alloys and Compounds, 190 (1993) L37-L38) describe micro-encapsulation of alloy powders with Cu, Cr, Co, Ni, Ni-Co, Ni-Sn and Ni-W. Scanning electron microscopy (SEM) showed good homogeneity of the completely encapsulated (completely covered or coated) metal layers.

[0007] Similar attempts to solve the degradation problems have been described in US patent specifications numbers 5 451 474 and 5 128 219, both of which relate to coating the whole surface of the hydrogen storage material with a barrier layer of a metal. Similarly, European patent specification number 198 599 describes a layer of metal covering

an amorphous alloy system.

[0008] In all these cases where the coating on the metal hydride-forming material is continuous, problems are experienced which affect the performance of the system. For example, in the Yunshin reference is described an accumulation of rare-earth metal occurring on some of the coated layers. The larger the concentration of rare-earth metal on the surface, the larger the decrease in the hydrogen absorption property of the alloy, which can be seen from the capacity decrease of the electrodes. In other cases, a continuous layer of barrier metal acts as a rate-determining step since, in use, hydrogen must first diffuse through the coating prior to effecting hydrogenation of the system.

[0009] It was thus a surprise to the present inventors when they found that an alloy powder when treated to provide the surface of at least some of the alloy particles with a discontinuous or partial deposit of one or more layers of at least one platinum group metal gave a hydrogen storage material with good air stability and resistance to overcharging damage, as well as recombination properties of any oxygen/hydrogen formed during charging. The capacity was essentially unaffected, and the kinetics of charge were at least as good after air exposure as is the base material when maintained in an oxygen-free environment.

[0010] Accordingly, the present invention provides a hydrogen storage material comprising hydride forming metallic particles and one or more platinum group metal(s), wherein the surface of at least some of the hydride-forming metallic particles have a discontinuous or partial deposit of one or more platinum group metal(s), which deposit is targeted to specific sites on the hydride-forming metallic particles by the reaction between said hydride forming metallic particles and a solubilised form of the PGM(s) under reducing conditions which comprise the presence of lattice hydrogen in the hydride forming metallic particles.

[0011] Suitable interface activation compositions are those which are understood to lower the activation energy for the transfer of hydrogen across the interface between the hydrogen storage material and another phase. Preferably, the interface activation composition comprises one or more platinum group metals.

[0012] The term "platinum group metal" (PGM) is well understood by a person skilled in the art and is defined in "The Condensed Chemical Dictionary", 7th Edition, Ed. Arthur and Elizabeth Rose, Reinhold Publishing Corporation, New York 1961, as meaning "A group of six metals, all members of group VIII of the period system. They include ruthenium, rhodium, palladium, osmium, iridium and platinum". The interface activation composition may include a transition metal having a reduction potential less than that of the hydride, which resists oxidation and which may act as a seed for the PGM, such as nickel or copper.

[0013] Preferably, the interface activation composition comprises palladium and/or ruthenium, more preferably ruthenium.

[0014] The term "discontinuous or partial deposit" should be interpreted as meaning that only part of the hydride-forming metallic particle surface is covered by the interface activation composition. The term "discontinuously coated" is to be understood as having an equivalent meaning in the context of this specification. There may be particles present which are not discontinuously coated, and which may either have no coating or may be continuously coated. However, it is preferred that in the range of from about 5% to about 100% of the hydride-forming metallic particles have a discontinuous coating of the interface activation composition, more preferably from about 50% to about 100%, especially from about 80% to about 100%.

[0015] The quantity of interface activation composition deposited onto the surface of the metallic particles may vary from trace amounts up to approximately 10% by weight of the total weight of the material (w/w). The term "trace amount" refers to concentrations less than 2000ppm, preferably less than 1000ppm, for example 100ppm or less. Preferably, particularly in the case where the interface activation composition comprises one or more PGMs, from about 0.02% to about 8%w/w, more preferably from about 0.08% to about 2%w/w of the or each PGM is deposited. From an economic viewpoint, the lower ranges are preferred. However, by using the discontinuous deposits according to the present invention, it has been found that the rates of hydrogen absorption/desorption do not vary significantly with thickness of the deposit, unlike in the case of the prior art continuous coatings. Hence, similar results are obtained, whether 8%w/w or 0.16%w/w is used, for example.

[0016] The hydride-forming metallic particles may be those of any hydride-forming metal or metal alloy known in the art.

[0017] Preferably, the hydride-forming metal is a metal which forms purely metallic hydrides or those hydrides of an intermediate nature (*ie* those possessing a degree of metallic bonding *eg* Mg); particularly preferred are Ti, Mg and Pd.

[0018] Suitably, the metal alloy is an intermetallic compound. Various types of these compounds will be known to a skilled person, but include Haucke type (AB_5), Laves Phase (AB_2), $CeNi_3$ type (AB_3), Ce_2Ni_7 type (A_2B_7), CsCl-CrB type (AB), Th_6B_{23} type (A_6B_{23}), $MoSi_2$ type (A_2B) and Ti_2Ni type (A_2B). A further description of these types of intermetallic compounds may be found in Libowitz, Electrochem. Soc. Proc., 92(5), pp 3-23, all of which are suitable for use in the present invention. Preferably, the intermetallic compounds are of the type AB_5 , AB or AB_2 . Examples of these types include $LaNi_5$, $TiNi$, $TiMn$ and $TiFe$ and ZrV_2 , $Zr(V_{0.33}Ni_{0.67})_2$, together with versions doped to control the pressure-composition-temperature plateau pressure and corrosion properties.

[0019] Another aspect of the present invention provides a method for producing an improved hydrogen storage

material by surface activation of the hydride-forming metal or metal alloy particles by applying a discontinuous coating or deposit of an interface activation composition to the hydride-forming metallic particles.

[0020] A further aspect of the invention therefore provides a process for preparing a hydrogen storage material comprising forming a discontinuous or partial deposit of one or more PGMs on hydride-forming metallic particles.

[0021] The formation or application of the discontinuous deposit may be carried out by methods analogous to those known in the art and will be illustrated below in terms of the preferred PGM discontinuous deposit of the present invention. In the case where more than one PGM is used, the discontinuous deposits can be formed sequentially or simultaneously. Preferably, the method is by reducing a solubilised form of the PGM(s) in the presence of the hydride-forming metallic particles. For example, a PGM salt such as a chloride, eg PdCl_4^{2-} or hexaminoruthenium(III) chloride, may be dissolved in a suitable solvent therefor, contacted with the hydride-forming metallic particles and, optionally in the presence of a complexing agent such as EDTA, reduced. The reduction may be effected by a reducing agent such as hydrazine hydrate or lattice hydrogen or *via* an exchange reaction with a hydrogen-containing or -forming substrate. Some of these processes may be termed electroless or exchange plating in the art.

[0022] If two or more PGMs are to be deposited, it is preferable that each individual PGM deposit forms discretely; however, the PGMs may also be co-precipitated to form a single discontinuous deposit comprising two or more PGMs. In the case where the discontinuous deposit comprises palladium and ruthenium, it is preferred to perform the palladium-depositing process first and thereafter form the ruthenium deposit.

[0023] More preferably, especially when discontinuously depositing palladium, the coating process is controlled by the presence of hydrogen in the hydride-forming metallic particles, *ie* lattice hydrogen. Accordingly, the process of the present invention more preferably comprises the step of introducing hydrogen into the hydride-forming metallic particles prior to the deposition step. Hydrogen-introduction may be carried out by any suitable process known to those skilled in the art, such as by gas phase hydrogenation (deposition of a reductant containing hydrogen (H_2 , gas phase)) or by electrochemical or chemical reduction, or by hydrogen decrepitation. The advantage of this hydrogenation step is that it obviates the need for addition of a reducing agent during the discontinuous depositing step and appears to result in a site-specific reaction, enabling the discrete particles of the discontinuous deposit (eg of PGM, eg of Pd) to be optimally sited.

[0024] For example, gas phase hydrogenation may be effected by exposing the hydride-forming metallic particles to H_2 whereby it is absorbed into the metal lattice, preferably at slightly elevated temperature and/or pressure. Alternatively, hydrogen-introduction may be effected by forming the metallic particles into a cathode and electrochemical means used, such as by using base electrolysis, to generate H_2 which is then absorbed at the cathode. A further alternative method is to mix the metallic particles with a suitable reducing agent such as sodium borohydride and allow the reducing agent to decompose on the particles' surface, whereby some hydrogen becomes incorporated.

[0025] A further alternative hydrogenation method is that of decrepitation, which is particularly preferred when it is also desirable to reduce the particles size of the hydride-forming metallic particles. However, such particle-size reduction may be carried out by any method known in the art, such as by mechanical means (eg crushing or pulverisation) as well as by hydrogen decrepitation (described further below). The particles are suitably treated to give an average particle size in the range of from about $5\mu\text{m}$ to about $100\mu\text{m}$, preferably from about $15\mu\text{m}$ to about $40\mu\text{m}$.

[0026] Preferably, however, the particles are subjected to one or more cycles of hydrogen decrepitation. This procedure typically comprises the following steps:

- (i) conditioning the hydride-forming metallic particles to facilitate the absorption of hydrogen thereby;
- (ii) desorption; and
- (iii) hydrogenation.

[0027] The desorption and hydrogenation steps may be carried out as many times as required. The greater the number of cycles, the smaller the resulting particles will be.

[0028] Preferably, the decrepitation process is carried out in a hydrogenation chamber and more preferably in the absence of oxygen.

[0029] The conditioning step may be undertaken by heating the particles up to 200°C and/or under pressure of up to about 10 bar (1MNm^{-2}).

[0030] The desorption step may be undertaken at a pressure below that of the equilibrium pressure for the particles, more preferably under vacuum, which acts as an indicator for the desorption process. Preferably, desorption is undertaken under elevated temperature, to about 150°C , to speed the process. The desorption step results in dehydrogenation of the particles, although some hydrogen usually remains in the lattice.

[0031] The hydrogenation step is preferably undertaken at room temperature but elevated pressure up to about 8 bar (0.8MNm^{-2}). It is preferred that the decrepitation process ends with a hydrogenation step so that deposition of the interface activation composition (preferably a PGM) takes place on hydrogen-loaded particles. It is preferred that the final desorption/dehydrogenation step be carried out during deposition.

[0032] Accordingly, the present invention further provides a method of preparing a hydrogen storage material, which method comprises:

- (a) introducing hydrogen into hydride-forming metallic particles (whereby lattice hydrogen is available for use as a reductant);
- (b) contacting the hydrogen-loaded particles thereby produced with a solubilised form of an interface activation composition, preferably in the absence of any further reducing agent (such as hydrazine hydrate); and, preferably simultaneously,
- (c) dehydrogenating, preferably under reduced pressure.

[0033] The hydrogen storage material of the present invention provides a source of hydrogen that does not require pressure vessels or cryogenic handling, and that has a volumetric density higher than that for liquid hydrogen. Such a source of hydrogen may be used in a variety of applications, such as those mentioned hereinbefore, for example rechargeable batteries, fuel cells, combustion engines, electronics, isotope separation, heat purification, catalytic dehydrogenation and hydrogenation reactions, and as a buffer capacity in any hydrogen handling process. Because the hydrogen storage material of the present invention provides hydrogen or energy in a cyclic fashion, at least two units comprising the material would be required in applications requiring a continuous source of hydrogen, one charging while the other is discharging.

[0034] For example, to manufacture an electrode comprising a material according to the invention, a suitable method comprises: hydrogenating hydride-forming metallic particles, forming a discontinuous deposit on the particles of a PGM and thereafter forming the resulting hydrogen storage material of the invention into an electrode. A preferred alternative is to form the electrode from the untreated particles (*ie* particles not having a deposit) and thereafter hydrogenate and discontinuously deposit PGM on the particles at the surface of the electrode. To manufacture an electrode or battery comprising a hydrogen storage material according to the invention, a suitable method comprises plasma-spraying a powder feed of hydride-forming metallic particles onto a (for example, Ni) substrate and hydrogenating then forming a discontinuous deposit of a PGM on the particles.

[0035] To manufacture a gas storage cell comprising a hydrogen storage material according to the invention, a suitable method comprises mixing hydride-forming metallic particles with an inert metal (such as Ni) powder, forming pellets thereof, hydrogenating the pellets, thereafter forming a discontinuous deposition of PGM on the pellets, and packaging the pellets into a suitable gas storage container.

[0036] A further aspect of the present invention provides a hydrogen electrode in which the hydrogen is stored using the hydrogen storage material of the present invention. A yet further aspect of the present invention provides a battery comprising a hydrogen electrode of the present invention.

[0037] The present invention will now be illustrated by way of the following examples, which are not intended to be limiting thereof.

EXAMPLE 1

Preparation of Alloy Particles having Discontinuous Pd/Ru Deposit

[0038] A sample of alloy, composition $\text{La}_{30.5}\text{Nd}_{1.68}\text{Pr}_{1.65}\text{Co}_{9.1}\text{Mn}_4\text{Al}_{1.88}\text{Ni}_{51.54}$ (Alloy A), was adsorbed/desorbed in hydrogen (referred to as hydrogen decrepitation) for 5 cycles (ending on desorption/dehydrogenation step) to give a fine powder with particle size *ca* 30 μm . The decrepitation powder was then discontinuously deposited, by a method analogous to that of Example 1, with Pd (4%w/w and 0.08%w/w, respectively) then Ru (4%w/w and 0.08%w/w, respectively) to give PGM coatings of 8% w/w total and 0.16% w/w total, respectively. Microstructural analysis by scanning electron microscopy (SEM), analysis by electron probe microanalysis (EPMA), inductively-coupled plasma (ICP) and X-ray photon spectroscopy (XPS) and hydrogenation kinetics by thermogravimetric analysis were performed.

[0039] A comparison of the kinetics of the discontinuously deposited Alloy A with the as-cast Alloy A are shown in Table 1 below.

TABLE 1

	Comparison Alloy A (as cast)	Composition 1 Alloy A 8wt% Pd/Ru (50/50)	Composition 2 Alloy A 0.16wt% Pd/Ru (50/50)
No. of H atoms/mol alloy	4.8	4.6	4.8

TABLE 1 (continued)

	Comparison Alloy A (as cast)	Composition 1 Alloy A 8wt% Pd/Ru (50/50)		Composition 2 Alloy A 0.16wt% Pd/Ru (50/50)	
H ₂ absorption time (mins)	9*	6		6	
H ₂ desorption time (mins)	60-120	80-100		80-100	
Air exposure time (mins)	10	150	450	150	450
No. of H atoms/mol alloy after exposure	Alloy poisoned	4.6	4.6	4.8	4.8
H ₂ absorption time after exposure (mins)		6	7	6	10
H ₂ desorption time after exposure (mins)		60-90	60-90	100-120	100-120

* Indicates the alloy required activation under temperature and pressure. The treated (discontinuously deposited) alloy required no activation treatment before hydrogenation occurred.

Cycle Life for Standard and Activated Ni-MH Batteries

[0040] Figure 1 shows the performance of the standard (Composition Alloy A as cast) hydride electrode material and Composition 2. Cells containing identical weight hydride electrodes were tested under a charge/discharge regime through to 100 cycles, monitoring cell performance as hours for voltage to fall to 1 volt at a discharge rate of 56mA, this being the rate consistent with a discharge at 0.2C₅A.

[0041] The discontinuously deposited material exhibits a relatively flat profile with little loss of performance. The standard material shows a greater loss of capacity and hence a reduced life.

Comparison of Charge Retention for Standard and Activated Ni-MH Batteries

[0042] Charge retention tests were carried out on standard and discontinuously deposited (Composition 2) hydride electrode batteries. Each cell was charged at 0.1C₅A for 16 hours and then left to stand for 28 days at 20°C ± 2°C. The cells were then discharged at 0.2C₅A and the ampere hour output measured to an end voltage of 1 volt. The data shown in Table 2 indicate a significant difference between the standard and discontinuously deposited hydride electrode cells.

TABLE 2

Cell	Mean initial duration (hours) at 0.2C ₅ to 1.0 V	Mean duration after 28 days open circuit (hours) at 0.2C ₅ to 1.0 V
Standard	3.68	1.11 (70% loss)
Composition 2	5.29	3.06 (42% loss)

EXAMPLE 2

Preparation by Hydrogen-Loading Method

[0043] A hydrogen storage material of the invention was prepared by a method analogous to that of Example 1 (alloy, hydrogen decrepitation) except that the decrepitation was undertaken for 5 cycles ending on a hydrogenation step.

The decrepitation powder was then discontinuously deposited with Pd then Ru by a method analogous to that of Example 1. The particles were dehydrogenated during the deposition step by applying a vacuum atmosphere (approx. 1×10^3 Pas). In analogous tests to those detailed above, it was found that the hydrogen storage materials of this example produced superior results to those of example 1, particularly in terms of their sorption characteristics after exposure to air.

Claims

1. A hydrogen storage material comprising hydride forming metallic particles and one or more platinum group metal(s), wherein the surface of at least some of the hydride-forming metallic particles have a discontinuous or partial deposit of one or more platinum group metal(s), which deposit is targeted to specific sites on the hydride-forming metallic particles by the reaction between said hydride forming metallic particles and a solubilised form of the PGM(s) under reducing conditions which comprise the presence of lattice hydrogen in the hydride forming metallic particles.
2. A hydrogen storage material according to claim 1, wherein the platinum group metal is palladium and/or ruthenium.
3. A hydrogen storage material according to claim 1 or claim 2, wherein the platinum group metal is or includes ruthenium.
4. A hydrogen storage material according to any preceding claim, wherein the one or more platinum group metal(s) comprises up to 10%w/w of the total weight of the material.
5. A hydrogen storage material according to claim 4, wherein the one or more platinum group metal(s) comprises in the range of from about 0.02% to about 8%w/w.
6. A hydrogen storage material according to claim 5, wherein the one or more platinum group metal(s) comprises in the range of from about 0.08% to about 2%w/w.
7. A process for preparing a hydrogen storage material according to any of claims 1 to 6, which comprises:
 - (a) introducing hydrogen into hydride-forming metallic particles;
 - (b) contacting the hydrogen-loaded particles thereby produced with a solubilised form of a platinum group metal; and
 - (c) dehydrogenating.
8. A process according to claim 7, which comprises:
 - (a) introducing hydrogen into a hydride-forming metallic alloy;
 - (b) contacting the hydrogen-loaded particles thereby produced with a soluble salt of a platinum group metal, such as PdCl_2 and/or $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$, in the absence of any further reducing agent; and, simultaneously,
 - (c) dehydrogenating under reduced pressure.
9. A process according to claim 7 or claim 8, wherein hydrogen is introduced into the hydride forming metallic particles by gas phase hydrogenation, electrochemical reduction, chemical reduction, or hydrogen decrepitation.
10. A process for preparing a hydrogen storage material according to any one of claims 1 to 6 comprising:
 - (i) reducing the particle size of hydride-forming metallic or metal alloy particles;
 - (ii) exposing the hydride-forming metal or metal alloy particles to a hydrogen atmosphere such that traces of hydrogen remain within the particles;
 - (iii) forming a discontinuous coating or deposit of an interface activation composition, by reacting the resulting particles with a solubilised form of one or more platinum group metal(s), on the hydride-forming metal or metal alloy particles.
11. A process according to claim 10, wherein the size of the particles is reduced to give an average particle size of $5\mu\text{m}$ - $100\mu\text{m}$.

12. A process according to claim 10 or claim 11, wherein the size of the particles is reduced by hydrogen decrepitation.
13. A hydrogen electrode in which hydrogen is stored using a hydrogen storage material according to any one of claims 1 to 6.
14. A rechargeable battery comprising a hydrogen electrode according to claim 13.

Patentansprüche

1. Wasserstoffspeichermaterial, das hydridbildende Metallteilchen und ein oder mehrere Metall(e) der Platingruppe umfasst, wobei die Oberfläche mindestens einiger der hydridbildenden Metallteilchen einen diskontinuierlichen oder teilweisen Überzug eines oder mehrerer Metalls (Metalle) der Platingruppe aufweisen, wobei der Überzug durch Reaktion zwischen den hydridbildenden Metallteilchen und einer solubilisierten Form des (der) Metalls (Metalle) der Platingruppe unter reduzierenden Bedingungen, die die Gegenwart von Gitterwasserstoff in den hydridbildenden Metallteilchen umfassen, auf spezielle Stellen auf den hydridbildenden Metallteilchen gerichtet ist.
2. Wasserstoffspeichermaterial nach Anspruch 1, wobei das Metall der Platingruppe Palladium und/oder Ruthenium ist.
3. Wasserstoffspeichermaterial nach Anspruch 1 oder 2, wobei das Metall der Platingruppe Ruthenium ist oder es umfasst.
4. Wasserstoffspeichermaterial nach einem der vorhergehenden Ansprüche, wobei das eine oder die mehreren Metall(e) der Platingruppe bis zu 10 % g/g des Gesamtgewichts des Materials ausmacht (ausmachen).
5. Wasserstoffspeichermaterial nach Anspruch 4, wobei das eine oder die mehreren Metall(e) der Platingruppe etwa 0,02 bis etwa 8 % g/g ausmacht (ausmachen).
6. Wasserstoffspeichermaterial nach Anspruch 5, das eine oder die mehreren Metall(e) der Platingruppe etwa 0,08 bis etwa 2 % g/g ausmacht (ausmachen).
7. Verfahren zur Herstellung eines Wasserstoffspeichermaterials nach einem der Ansprüche 1 bis 6, das die folgenden Stufen umfasst:
 - (a) Einführen von Wasserstoff in hydridbildende Metallteilchen;
 - (b) Inberührungbringen der mit Wasserstoff beladenen Teilchen, die dabei erhalten wurden, mit einer solubilisierten Form eines Metalls der Platingruppe und
 - (c) Dehydrieren.
8. Verfahren nach Anspruch 7, der die folgenden Stufen umfasst:
 - (a) Einführen von Wasserstoff in eine hydridbildende Metalllegierung;
 - (b) Inberührungbringen der mit Wasserstoff beladenen Teilchen, die dabei erhalten wurden, mit einem löslichen Salz eines Metalls der Platingruppe, beispielsweise PdCl_2 oder $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$, in Abwesenheit eines beliebigen weiteren Reduktionsmittels und gleichzeitig
 - (c) Dehydrieren unter verringertem Druck.
9. Verfahren nach Anspruch 7 oder 8, wobei Wasserstoff durch Gasphasenhydrierung, elektrochemische Reduktion, chemische Reduktion oder Wasserstoffdekrepitation in die hydridbildenden Metallteilchen eingeführt wird.
10. Verfahren zur Herstellung eines Wasserstoffspeichermaterials nach einem der Ansprüche 1 bis 6, das die folgenden Stufen umfasst:
 - (i) Reduzieren der Teilchengröße der hydridbildenden Metall- oder Metalllegierungsteilchen;
 - (ii) Einwirkenlassen einer Wasserstoffatmosphäre auf die hydridbildenden Metall- oder Metalllegierungsteilchen derart, dass Spuren von Wasserstoff in den Teilchen verbleiben;
 - (iii) Ausbilden eines diskontinuierlichen Belags oder Überzugs einer Grenzflächenaktivierungszusammensetzung

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zung durch Umsetzen der erhaltenen Teilchen mit einer solubilisierten Form eines oder mehrerer Metalls (Metalle) der Platingruppe auf den hydridbildenden Metall- oder Metalllegierungsteilchen.

11. Verfahren nach Anspruch 10, wobei die Größe der Teilchen verringert wird, um eine durchschnittliche Teilchengröße von 5 µm bis 100 µm zu erhalten.

12. Verfahren nach Anspruch 10 oder 11, wobei die Größe der Teilchen durch Wasserstoffdekreption verringert wird.

13. Wasserstoffelektrode, worin Wasserstoff unter Verwendung eines Wasserstoffspeichermaterials nach einem der Ansprüche 1 bis 6 gespeichert ist.

14. Wiederaufladbare Batterie, die eine Wasserstoffelektrode nach Anspruch 13 umfasst.

Revendications

1. Matériau stockant l'hydrogène comprenant des particules métalliques formant hydrure et un ou plusieurs métaux du groupe du platine, dans lequel la surface d'au moins certaines des particules métalliques formant hydrure présente un dépôt discontinu ou partiel d'un ou plusieurs métaux du groupe du platine, lequel dépôt est ciblé vers des sites spécifiques sur les particules métalliques formant hydrure par la réaction entre lesdites particules métalliques formant hydrure et une forme solubilisée de MGP (métaux du groupe du platine) dans des conditions de réduction qui comprennent la présence d'hydrogène formant réseau dans les particules métalliques formant hydrure.

2. Matériau stockant l'hydrogène selon la revendication 1, dans lequel le métal du groupe du platine est le palladium et/ou le ruthénium.

3. Matériau stockant l'hydrogène selon la revendication 1 ou la revendication 2, dans lequel le métal du groupe du platine est ou comprend le ruthénium.

4. Matériau stockant l'hydrogène selon l'une quelconque des revendications précédentes, dans lequel le ou les groupes métalliques du groupe du platine comprennent jusqu'à 10 % en p/p du poids total du matériau.

5. Matériau stockant l'hydrogène selon la revendication 4, dans lequel le ou les métaux du groupe du platine se situent dans la plage comprise entre environ 0,02 % et 8 % p/p.

6. Matériau stockant l'hydrogène selon la revendication 5, dans lequel le ou les métaux du groupe du platine se situent dans la plage comprise entre environ 0,08 % et environ 2 % p/p.

7. Procédé pour préparer un matériau stockant l'hydrogène selon l'une quelconque des revendications 1 à 6, qui comprend les étapes consistant à :

(a) introduire de l'hydrogène dans des particules métalliques formant hydrure ;

(b) mettre en contact les particules chargées d'hydrogène ainsi produites avec une forme solubilisée d'un métal du groupe du platine ; et

(c) effectuer une déshydrogénation.

8. Procédé selon la revendication 7, comprenant :

(a) l'introduction d'hydrogène dans un alliage métallique formant hydrure ;

(b) la mise en contact les particules chargées d'hydrogène ainsi produites avec un sel soluble d'un métal du groupe du platine, comme le PdCl_2 et/ou le $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ en l'absence de tout autre agent réducteur ; et, simultanément,

(c) la déshydrogénation sous pression réduite.

9. Procédé selon la revendication 7 ou la revendication 8, dans lequel l'hydrogène est introduit dans les particules métalliques formant hydrure par hydrogénation en phase gazeuse, réduction électrochimique, réduction chimique ou décréption à l'hydrogène.

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10. Procédé pour préparer un matériau stockant l'hydrogène selon l'une quelconque des revendications 1 à 6 comprenant :

(i) la réduction de la taille de particule des particules métalliques formant hydrure ou des particules d'alliages métalliques ;

(ii) l'exposition des particules métalliques formant hydrure ou des particules d'alliages métalliques à une atmosphère d'hydrogène de telle sorte que des traces d'hydrogène restent à l'intérieur des particules ;

(iii) la formation d'un dépôt ou d'un revêtement discontinu d'une composition d'activation d'interface, en faisant réagir les particules obtenues avec une forme solubilisée d'un ou plusieurs métaux du groupe du platine, sur les particules métalliques formant hydrure ou les particules d'alliages métalliques.

11. Procédé selon la revendication 10, dans lequel la taille des particules est réduite pour donner une taille de particule moyenne comprise entre 5 μm et 100 μm .

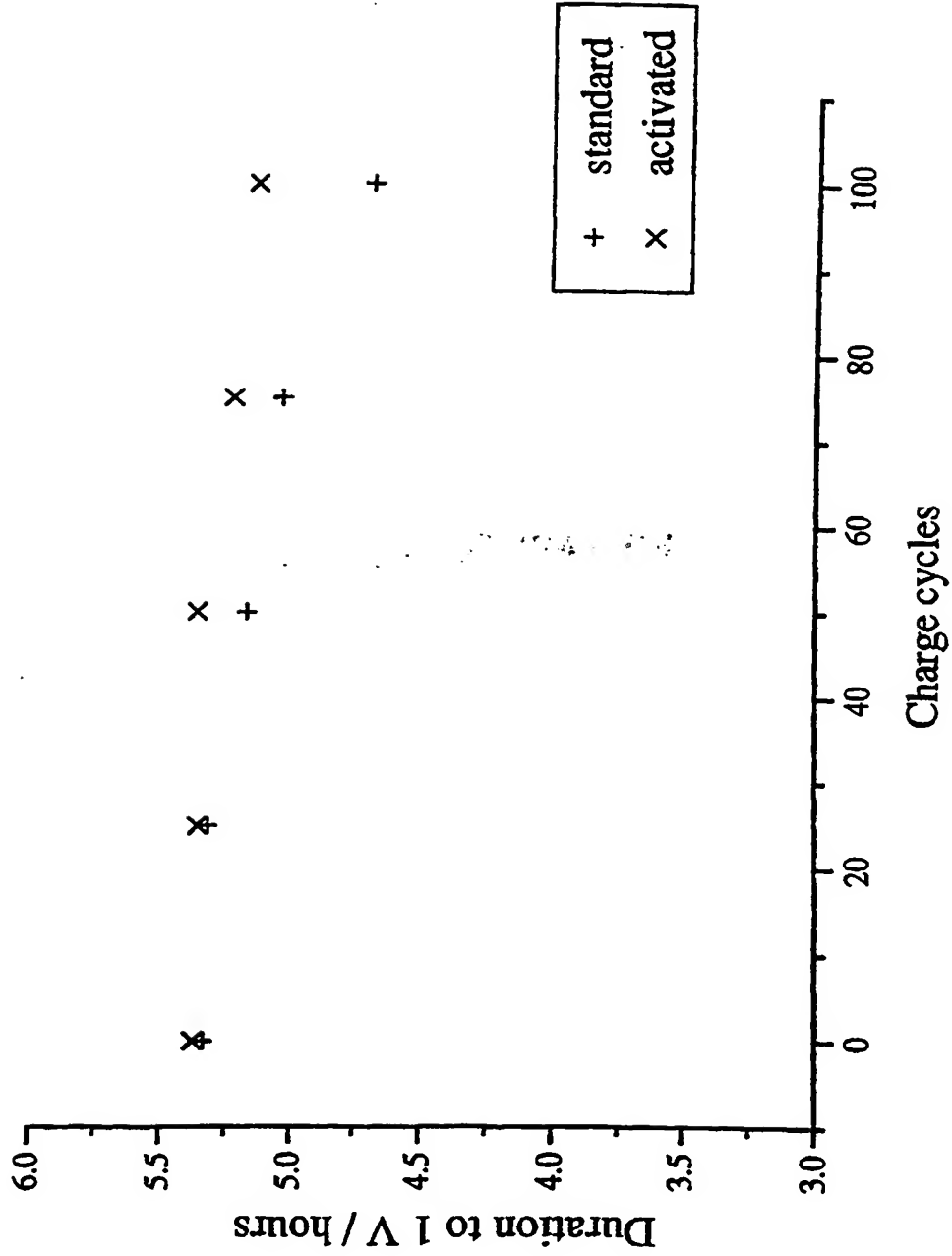
12. Procédé selon la revendication 10 ou la revendication 11, dans lequel la taille des particules est réduite par dé-crépitation à l'hydrogène.

13. Electrode à hydrogène dans laquelle l'hydrogène est stocké en utilisant un matériau stockant l'hydrogène selon l'une quelconque des revendications 1 à 6.

14. Pile rechargeable comprenant une électrode à hydrogène selon la revendication 13.

FIGURE 1

Cycle life for standard and activated NiMH batteries



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